ACETIC ACID PRODUCTION
FROM MARINE ALGAE

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Section 1

SUMMARY

The overall goals of this program are:

1. To develop an economically competitive process for producing acetic acid from biomass for the purpose of sparing petroleum for other uses.
2. To evaluate marine algae as a potential source of biomass.
3. To document the feasibility of running fermentations in fixed packed bed fermenters.

In the first quarter of work, several positive results have been generated which will contribute to the realization of these goals. First, it has been demonstrated that marine algae can be fermented to acetic acid. Initial rates of up to 168 meq/l day have been observed. These rates are substantially in excess of the 47 meq/l day used in the economic projections. Also, using marine algae as a substrate acid levels have been generated equivalent to the highest reported with other substrates. It has also been demonstrated that a 4 foot fixed packet bed fermenter may be operated with marine algae as a substrate at 20% solids; or 200 meq/l.

Section 2

INTRODUCTION

The objects of this work are to develop an economically competitive process for producing acetic acid from biomass and to evaluate marine algae as a biomass. It is known that in the anaerobic digestion of organic matter to methane that acetic acid is an intermediate, and conversion will stop at the organic acid stage unless careful control of the digester is exercised. The reaction for conversion of a hexose to acetic acid may be represented as:

However, it has been demonstrated that certain anaerobic bacteria (e.g., *Clostridium Thermoaceticum*) convert hexose to acetic acid according to the reaction:

It is also known that anaerobic bacteria exist which convert CO_2 and hydrogen to methane:

and that acetic acid can be detected in the liquid phase. It has not been demonstrated that acetic acid is an intermediate in this reaction, but it is likely. It is, therefore, likely that even with a mixed culture of bacterial anaerobes that more than two acetic acid molecules will be obtained from each hexose molecule, and percent yields will be calculated based on three acetic acid molecules/hexose as 100%.

It was anticipated that since acetic acid is an intermediate in methane formation that its rate of production would be greater than or equal to methane formation. This anticipation has been borne out by initial experiments, which will be discussed in more detail later.

It was also anticipated that because of its higher yield and selling price on a weight basis that distinct advantages were available to acetic acid production over methane production provided relatively inexpensive isolation techniques could be employed. The economics of acetic acid production are discussed in some detail later.

Marine algae (seaweed) are a very interesting form of biomass. In addition to having high yields per acre of otherwise relatively unproductive area, their organic matter consists largely of water-soluble polysaccharides instead of the cellulose of land-based biomass. In fact, Chondrus Crispus a red alga contains only 2% cellulose. These polysaccharides should be readily available to the required hydrolytic enzymes if present. It is thought that cellulose hydrolysis is the rate-limiting step in fermentation or digestion of land-based biomass. It is, therefore, likely that improved rates may be obtained from marine algae over land-based biomass.

Another point to consider is the absence of lignin in marine algae. Lignin in land-based biomass impedes cellulose hydrolysis as well as being refractory to these processes itself.

Some of the negative aspects of marine algae as biomass are that many have high ash contents, which make disposal a chore as well as may effect bacterial action because of hypertonicity. The biggest negative aspect is that no estimate of the production cost of marine algae is currently available.

The species of marine algae selected for initial study is Chondrus Crispus, a red alga of commercial interest because of its carrageenan content.

Carrageenan is a sulfonated polygalactose which is an effective thickening agent, particularly with milk. Analysis of Chondrus Crispus currently on hand is:

Table 2.1

ANALYSIS OF CHONDRUS CRISPUS

Moisture	27% weight
Volitile Solids	66% moisture free basis
Aqueous Extractible Solids	30% moisture free basis, 45% of volitile solids

The primary advantage of Chondrus Crispus (irish moss) is that it is available in commercial quantities on the East Coast.

In order to devise a practical process for converting marine algae to acetic acid, the experimental program must address four questions:

1. What should the fermeter look like?
2. What should the fermenter contain? Substrate? Nutrients? Innoculum?
3. How should the fermenter be operated? High acid, low acid? Mesophilic? Thermoplilic?
4. How much will the acid cost?

The program as presented in the bar chart in Figure 2.1 is designed to address these questions.

ERD-4 PROGRAM

Section 3

FERMENTATION EXPERIMENTS

3.1 The Effect of Solids Level and Substrate/Sludge Ratio On Acetic Acid Production

A series of six unstirred fermenters were set up containing different solids levels and ratios of substrate (Chondrus Crispus) to sewage sludge. The sewage sludge was obtained from the Nut Island Sewage Treatment Plant in Quincy, Massachusetts. The results of these six experiments along with the % solids and substrate/sludge ratio are presented in Table 3.1. The acetic (A) propionic (P), butyric (B), and Valeric acid (V) concentrations in miliequivalents/liter were determined by gas chromatography using a 2 foot Porepack QS column. The total acid concentration (T) is the sum of individual acid concentrations. The ratio of acetic acid to total acid (A/T) is also given. The total reducing equivalents (R) is obtained from the equation:

$$R = A + 1.75 P + 2.5 B + 3.25 V$$

The basis for this equation is the following set of reactions:

The percent conversion (C) is based on the assumption that all of the measured volatile solid material is hexose and that hexose is converted to three acetic acid molecules at 100% conversion.

The data in Table 3.1 precipitate several observations. The first is that at long times the acetic acid to total acid ratio (A/T) is higher at lower sludge levels. Table 3.2 presents the A/T ratios after 26 days for each of the six experiments.

A second observation is that the total acid levels appear to increase asymptotically with time; that is to say, obey a differential equation of the form:

$$\frac{\partial C}{\partial \tau} = K(C_{\infty} - C) \quad (3.1)$$

A solution for this equation is:

$$-\ln (C_{\infty} - C) = K\tau + \text{Const.} \quad (3.2)$$

since at $\tau = 0$ $C = 0$, $\text{const} = \ln C_{\infty}$

$$\ln \left(\frac{C_{\infty} - C}{C_{\infty}} \right) = -K\tau \quad (3.3)$$

Figure 3.1 presents as an example the first eight days worth of data from experiment 4 presented in this way. From such a plot the rate constant k may be obtained. From equation 3.1 it can be seen that the initial rate, the rate at $C=0$ is:

$$\left(\frac{\partial C}{\partial \tau} \right)_0 = K C_{\infty}$$

The initial rates determined in this way for the experiments using 90/10 substrate/sewage sludge ratios are presented in Table 3.3. It is interesting to note that the initial rate increases with increasing solids concentration.

That the data appear to follow equation 3.1 does not resolve one ambiguity in the mechanistic interpretation of these results. This type of behavior can be explained either by product inhibition or by depletion of substrate. If substrate depletion were the cause of this behavior one would expect C^∞ to be proportional to solids content. The data in Table 3.3 indicate that this is the case at low solids levels but not at high solids levels. It is apparent that in the solids range of interest (10%-20%) that the first order kinetic behavior is due to product inhibition.

A second set of three experiments were run to extend the observation of higher ultimate A/T ratios at lower substrate/sludge ratios. The experiments were run at 15% solids based on the promising results of the first set of experiments. The first unstirred fermenter was a duplicate of experiment 5 of the first set. The second substituted 10% digester effluent from 500 CSTR's operating on Gracillaria, a red alga, and Ulva lactuca, a green alga. The third fermenter contained 1% sewage sludge and 1% digester effluent. The results are presented in Table 3.4.

Fermenter 1 behaved as before, reaching a C^∞ of ~ 130 meq/l in 4-6 days. However, more measurements of acid production were made at short times to give a better idea of the A/T ratio as a function of time or total acid concentration. Table 3.5 tabulates these results separately. At short times the A/T ratio was as high as 0.9, but in 5 days it had dropped to the 0.55 observed in earlier experiments.

Fermenter 3 behaved similarly, but fermenter 2 behaved quite differently. Figure 3.2 presents total acid concentration vs. time, and Figure 3.3 presents $\ln (C^\infty - C)$ vs. time for this experiment.

The C^∞ value (220 meq/l) is significantly higher than any obtained previously, as is the initial rate. An analysis of these fermenters for free ammonium ion using a specific ion electrode indicated that

fermenters 1 and 3 were deficient in this nutrient. The results are presented in Table 3.6.

Table 3.6

NH₄⁺ Concentration in Fermenter

<u>Fermenter No.</u>	<u>NH₄⁺ CONC PPM</u>
1	20
2	85
3	19

An experiment is currently in process to determine whether this difference in ammonium ion concentration is responsible for the difference in performance of fermenter 2 vs. fermenters 1 and 3.

It is important to determine what is the total available reducing equivalent of an organic substrate for acid production. To determine this for Chondrus Crispus, a series of 9 unstirred fermenters were set up. The idea is to run these fermenters at sufficiently low solids to ensure that substrate depletion will occur before product inhibition. Each fermenter was inoculated with one drop of digester effluent to ensure that all of the reducing equivalents obtained were from the substrate. The composition of these fermenters and the results to date are presented in Table 3.7. Because of the low solids levels and small quantities of inoculation employed, the conversion rates in these fermenters are extremely slow. Hopefully, these fermentations will be completed during the coming quarter. In the case of the celka floc controls, these have been noted to produce methane during the early stages of fermentation before the pH drops, which may explain some of their erratic behavior.

Figure 3.1

Figure 3.2

TOTAL ACID CONCENTRATION VS TIME
15% SOLIDS - 90% CHONDRUS CRISPUS
10% DIGESTER EFFLUENT

LN $C_{\infty} - C_t$ VS TIME
 15% SOLIDS - 90% CHONDRUS CRISPUS
 10% DIGESTER EFFLUENT

Table 3.1

THE EFFECT OF SOLIDS AND SUBSTRATE/SLUDGE
RATIO ON ACETIC ACID PRODUCTION

Expt.No.	% Solids	Substrate/Sludge	Day	A	P	B	V	T	A/T	R	Y
1	4.0	0/100	0	75	8	2	< 1	18	42	29	6.04%
			1	23	42	3	0	68	34	104	21.67%
			2	35	30	6	2	73	48	109	22.70%
			4	34	30	4	< 1	69	49	99	20.63%
			6	34	30	4	4	72	47	109.5	22.81%
			8	30	30	6	2	68	44	104	21.67%
			26	40	50	9	2	101	40	156.5	32.60%
			50	40	62	12	8	122	33	204.5	42.60%
2	2.5	90/10	0	2	5	< 1	< 1	8	25	15	5.55%
			1	3	2	4	0	9	33	16.5	5.97%
			2	23	13	12	0	48	48	76	27.39%
			4	13	11	4	0	28	46	42	15.28%
			6	15	17	4	0	36	42	55	19.80%
			8	18	12	5	< 1	36	50	54	19.56%
			26	27	12	8	2	49	55	74.5	26.94%
			50	17	10	9	7	43	40	80	28.84%
3	5.0	90/10	0	2	5	< 1	< 1	8	25	15	2.78%
			1	8	7	4	0	19	41	30	5.47%
			2	20	14	2	0	36	55	49.5	8.95%
			4	26	17	4	0	47	55	66	11.89%
			6	13	18	6	0	37	35	59.5	10.76%
			8	38	20	10	2	70	54	104.5	18.89%
			26	45	20	18	2	85	53	131.5	23.77%
			50	90	23	16	8	137	66	196	35.48%
4	10.0	90/10	0	5	5	< 1	< 1	10	50	18	1.66%
			1	30	15	2	0	47	64	61	5.54%
			2	42	20	10	< 1	73	58	105	9.46%
			4	44	20	17	2	83	53	128	11.57%
			6	50	19	20	5	94	53	149.5	13.51%
			8	53	21	18	5	97	55	153	13.83%
			26	55	18	22	7	102	54	164	14.85%
			50	59	20	25	12	126	55	195.5	17.67%
5	15.0	90/10	0	12	5	< 1	0	17	71	23	1.37%
			1	42	23	4	0	69	61	92	5.56%
			2	53	24	19	1	97	55	146	8.78%
			4	60	25	34	0	119	50	189	11.37%
			6	66	22	35	9	132	50	221	13.33%
			8	63	21	35	10	129	49	220	13.24%
			26	80	20	30	12	142	46	229	13.80%
			50	111	25	29	14	179	62	273	16.44%

Table 3.1 (continued)

Expt. No.	% Solids	Substrate/Sludge	Day	A	P	B	V	T	A/T	R	Y
6	10.0	60/40	0	13	9	1	< .5	23	57	32	2.83%
			1	25	18	4	0	47	53	66.5	5.85%
			2	50	47	6	2	105	48	154	13.52%
			4	54	65	12	0	131	41	198	17.38%
			6	60	73	13	7	153	39	243	21.36%
			8	34	50	8	2	90	38	148	13.01%
			26	78	57	13	10	158	49	243	21.34%
			50	93	60	12	8	173	54	254	22.33%

Table 3.2

RATIO OF ACETIC TO TOTAL ACID AS A FUNCTION
OF SEWAGE SLUDGE CONCENTRATION

<u>EXPT. No.</u>	<u>% SOLIDS</u>	<u>SUBSTRATE*/SLUDGE</u>	<u>A/T RATIO - DAY 26</u>
1	4.0	0/100	.40
2	2.5	90/10	.55
3	5.0	90/10	.53
4	10.0	90/10	.55
5	15.0	90/10	.56
6	10	60/40	.49

* CHONDRUS CRISPUS

Table 3.3

EFFECT OF % SOLIDS ON RATES

90% CHUNDRUS CRISPUS/10% SEWAGE SLUDGE

<u>% Solids</u>	<u>K Day⁻¹</u>	<u>C[∞] meq/l</u>	<u>Initial Rate KC[∞]</u>
2.5	0.275	40	11
5.0	0.24	80	19
10.0	0.42	100	42
15.0	0.61	130	79

Table 3.4

EFFECT OF INNOCULUM ON ACETIC ACID PRODUCTION

15% SOLIDS - CHONDRUS CRISPUS

<u>Fermenter No.</u>	<u>Innoculum</u>	<u>Ratio</u>	<u>Time</u>	<u>A</u>	<u>P</u>	<u>B</u>	<u>V</u>	<u>T</u>	<u>A/T</u>	<u>R</u>	<u>C</u>
1	Sewage Sludge	90/10	0 hrs	32	3.5	3	0	38.5	83	45.5	3
			2	24	3	0	0	27	89	29	2
			4	23	2.5	0	0	25.5	90	27	2
			6	28	9	0	0	37	76	44	3
			8	33	8.5	1	0.5	43	77	52	3
			28	51	15	19	2.0	87	59	131	8
			49	67.5	33	37	0	137.5	49	218	13
			58	59	14	35.5	0	108.5	54	172	10
			75	59	13	35	0	107	55	169	10
			102	70	15	35	0.5	121	58	185	11
			129	79	16	38.5	3	139	57	213	13
			149	65.5	125	35	4	117	56	188	11
2	Digester Effluent	90/10	0	17.5	10	3	0	30.5	57	42.5	2
			2	27.5	10	0	0	37.5	73	45	2
			4	30	9	0	0	39	77	46	2
			6	33	10	0	0	43	77	50.5	2
			8	34.5	12.5	2.5	1.0	50.5	68	66	3
			28	113	22	9	0	144	78	174	8
			49	117.5	22	30	0	169.5	69	231	11
			58	127.5	22	40	0	190	67	266	12
			75	145.5	23	52	0	220.5	66	316	15
			102	135.5	27.5	71	3	237	57	371	17
			129	148	27.5	71	1	247.5	60	377	17
			149	140	25	60	4	229	61	347	16
3	Digester Effluent & Sewage Sludge	99/1	0	12.5	2	0	0	14.5	86	16	1
			2	23	2	0	0	25	92	26.5	2
			4	22	2.5	0	0	24.5	90	26.5	2
			6	23	2.5	0	0	25.5	90	27	2
			8	27.5	4	2	.3	34	81	46.5	2.5
			28	55	10	20	0	85	65	122	7
			49	62	11	37	0	110	56	174	11
			58	62	9	37.5	0	108.5	57	171.5	11
			75	63	10	39	0	112	56	178	11
			102	72	11	44.5	0	127.5	56	203	12
			129	55	6	35	0	96	57	153	9

Table 3.5

RATIO OF ACETIC TO TOTAL ACID AS A FUNCTION OF TIME
15% SOLIDS, 90% CHONDRUS CRISPUS, 10% SEWAGE SLUDGE

<u>TIME IN HOURS</u>	<u>A/T</u>
0	.83
2	.89
4	.90
6	.76
8	.77
28	.59
49	.49
58	.54
75	.55
102	.58
129	.57
149	.56

Table 3.7

DETERMINATION OF TOTAL REDUCING EQUIVALENTS

Fermenter	% Solids	Substrate	Time	A	P	B	V	T	A/T	R	C
A	0.25	Chondrus	0	4	2.5	2.5	1.3	10.3	39	19	69.35%
			47	2	.5	.5	.25	3.25	62	5	18.25%
			144	2.5	<1	<1	0	4	61	6	21.90%
B	0.50	Chondrus	0	3	2	1	<1	7	44	12	21.90%
			47	2.4	.5	1	.2	4	59	6	10.95%
			144	3	<1	2	0	6	52	9	16.43%
C	1.0	Chondrus	0	2	1.8	.5	.25	4.5	44	7	6.39%
			47	2.5	.8	2	.2	5.5	45	9.5	8.70%
			144	4	1	2.5	0	7.5	53	12	10.95%
D	1.5	Chondrus	0	2.3	2	1	<1	6	38	11	6.69%
			47	3	.8	4	.2	8	37.5	15	9.13%
			144	5	2	3.5	0	10.5	47.5	17	10.34%
E	2.5	Chondrus	0	1.5	1	<1	.2	3.5	43	6	2.19%
			47	4	1	10.5	.25	16	26	33	12.50%
			144	6	1.5	8	0	15.5	39	29	10.59%
F	0.25	Celka-Floc	0	1	1	<.5	<.1	2.5	40	4	9.60%
			47	1	.5	.5	0	2	50	3	7.20%
			144	<1	<1	<1	<1.2	3	33	7	16.80%
G	0.5	Celka-Floc	0	1	1	<.5	.2	2.5	40	4	4.80%
			47	1.75	.5	.5	.2	3	60	4.5	5.40%
			144	<1	<1	0	0	1.5	50	2	2.40%
H	0.25	Carrageenan	0	1	1	<1	<1	3.5	30	7	16.80%
			47	1	.5	.5	0	2	50	3	7.20%
			144	<1	<1	<1	0.2	2.5	40	4	9.60%
I	0.5	Carrageenan	0	1	<1	<1	<1	2	50	2	2.40%
			47	2	1	.75	.2	4	50	6	7.20%
			144	3	1	<1	0	5	60	7	8.40%

Section 4

FERMENTER DESIGN

4.1 Design Considerations - Acid Removal

In order to operate a fermenter to convert marine algae to acetic acid it is necessary to remove the acid as it is formed. The concept presented in proposing this work is to use a packed bed fermenter with circulating liquid. The acetic acid may be removed from the liquid phase during recirculation. Although a detailed design of the removal system is not a part of this contract, a usable concept will have to be developed and employed for experimental purposes.

The fermenter can be operated either at a high acid level or a low acid level. A high acid level may be beneficial in separating the product economically by solvent extraction (e.g., the Othmer or Hydrosience process), but perhaps with a reduction in rate due to product inhibition and a lower A/T ratio. Low acid concentrations would obviate these difficulties but would require separation as a salt with subsequent regeneration by mineral acid. The separation may be accomplished by ion exchange, membranes, or organic solvents, but in each case an equivalent of base and an equivalent of acid will be required for each equivalent of organic acid.

For current experimental purposes, a system based on extraction of the organic acid into an organic solvent and subsequent reextraction into base is needed. The desired characteristics of a suitable organic solvent are (1) low water solubility, (2) reasonably high partition coefficient for acetic acid, (3) relatively non-biodegradable, and (4) non-toxic to microorganisms. Two classes of solvents which meet all of these criteria except the of high partition coefficient are aliphatic hydrocarbons and "Freon" type fluorocarbons. The aliphatic hydrocarbons are immiscible

with glacial acetic acid and are, therefore, unsuitable. Freons with available data are completely miscible with glacial acetic acid.

4.2 Measurement of Properties of Potential Extractants

Measurements were made of the partition coefficient of organic acid in a 1% solution with Freon TF ($\text{Cl}_2\text{FC} - \text{CCl F}_2$). Approximately 1% solutions of acetic, propionic, butyric, and valeric acid in water were prepared. A 50 ml aliquot of each solution was titrated using 0.5N NaOH and phenolphthalein as an indicator. Additional aliquots of each acid were extracted with an equal volume of Freon TF by adding each solution to a separatory funnel, shaking for 30 seconds, letting the layers separate, shaking for 30 seconds and letting the layers separate once again, then titrating the aqueous layer as before. The results are presented in Table 4.1

Table 4.1

DETERMINATION OF PARTITION COEFFICIENTS OF ACETIC
PROPIONIC, BUTYRIC, AND VALERIC ACIDS WITH FREON TF

<u>Acid</u>	<u>Initial Conc.</u>	<u>Final Conc.</u>	$K \left(\frac{\text{CI} - \text{CF}}{\text{CI}} \right)$
Acetic	0.173 M/l	0.173 M/l	0
Propionic	0.134 M/l	0.128 M/l	0.047
Butyric	0.110 M/l	0.079 M/l	0.392
Valeric	0.093 M/l	0.031 M/l	2.00

It appears from these results that Freon TF is suitable only for removing the higher organic acids from the fermenter.

Another possibility for an extraction solvent is the use of trioctyl phosphine oxide dissolved in either Freon TF or an alkane. The use of this material, TOPO, as an extractant is discussed and referenced in the next section. Preliminary results with a 10% solution of TOPO in Freon TF indicated no reduction in acid formation in its presence, and a partition coefficient of 0.4 for acetic acid.

4.3 Flow Characteristics of Packed Bed Fermenters Containing Chondrus Crispus.

Some preliminary results on solids levels and flow characteristics of the packed bed fermenter are available from initial experiments with the packed bed fermenter operated with Chondrus. It was determined that the solids loading attainable by simply pouring dry, as received, Chondrus into the fermenter and adding sludge as 10% of total solids was 200 g/l or 20%. No attempt was made at compaction during filling. The column was then made up to volume with water and tested at various pumping rates. A Jabsco pump (rigger vanes, positive displacement, maximum $\Delta P \approx 7$ psi) with a variable drive, capable of pumping at 150 to 800 ml/min was then used to circulate liquid through the bed. At a flow rate of 150 ml/min, observed pressure drop varied between 2.3 and 3.2 psi one day after pumping was initiated. At a flow rate of 500 ml/min, the maximum pressure drop of 7 psi was attained. These pumping rates correspond to superficial velocities of .06 cm/sec (2.2 M/hr) to .167 CM/sec (6.0 M/hr). Linearity of pressure drop with flow rate would indicate that the bed under these conditions was relatively incompressible. At this time it became apparent that such high superficial velocities were unnecessary, and a 40/1 reducer was put on the pump head. The pump was then operated at a flow rate of 12-14 ml/min to give a superficial liquid velocity of $\sim 5 \times 10^{-3}$ cm/sec, or ~ 0.2 M/hr, at which point the pressure drop was not measurable (≤ 0.2 psig).

Section 5

PRELIMINARY PROCESS DESCRIPTION AND ECONOMIC ANALYSIS

5.1 Process Description

The process to produce acetic and other organic acids from marine algae will be similar to that for the conventional anaerobic digestion of municipal wastes, outlined in Refs. 5.1-5.3. The following basic unit operations will be required.

1. Collection of algae at a receiving station.
2. Shredding of algae biomass. This shredding step is necessary to provide a material suitable for packed bed digestion. Because of the nature of algal biomass, it is anticipated that shredding be accomplished by equipment similar to the secondary shredders of Ref. 5.1.
3. Digestion of algae, which may have added sewage sludge, in a packed bed digester. Acids formed during digestion will be continuously removed in an external subsystem and purified. Liquid is recycled to the packed bed system after the acid removal step.
4. Return of the spent residue, containing nutrients, to the algal growth system.

5.2 Material Flows, Process Performance and Yield

As the basis for evaluating the performance of a full-scale facility for generation of acetic and other organic acids from marine algae, it is assumed that algal input to the facility will be 1000 Tons/day on a dry weight basis. The algae is 75% organics and 25% ash. Sewage sludge

is also an input to the plant, providing the microbial nutrients required for acid production, at 1000 Tons/day. The sludge contains 5% organic solids. This nominal plant size and input are similar to those chosen for evaluating the alternative but similar process of fermenting municipal wastes to methane.

In estimating organic acid yield, it will be assumed that 50% by weight of organic input to the facility will be converted to acids. This yield would be obtained, for example, if 60% of organics were biodegradable and 83% were actually converted to acids under plant conditions (weight yield will be close to 1:1). With an 800 Ton/day organic input, acetic/organic acid output will be 400 Tons/day or 131,000 Tons/year at a 90% plant service factor.

5.3 Estimate of Packed Bed Digester Size

A critical factor in the over-all economics of acid production will be the size of reactor required to carry out the conversion. Reactor size is fixed by the volumetric productivity and the desired output rate. For purposes of this evaluation, it will be assumed that the value for productivity which can be attained is that implicit from representative productivities observed with methane production from solid waste. Higher productivities under mesophilic conditions are in the order of $1 \text{ ft}^3 \text{CH}_4 / \text{ft}^3 \text{ digester volume} \cdot \text{day}$. A productivity of $1 \text{ ft}^3 / \text{ft}^3 \text{ day}$ would be attained by production and subsequent digestion of acetic acid as an intermediate at a rate of $47 \text{ mmol/l} \cdot \text{day}$. (It is important to note that production of methane at the stated rate must necessarily involve production of intermediate acids at this rate, supporting the likelihood of attaining this productivity in a process to generate acids.) With a daily production of 400 U.S. Tons of acetic acid and this volumetric productivity, the total reactor volume required may be shown to be $4,550,000 \text{ ft}^3$.

At a 12% initial solids loading, judged attainable in a packed bed reactor, and a 1050 Ton/day charge of dry solids from algae and sludge, residence time for the solids will be near 17 days. This value for residence time is also typical of processes for generation of methane from solid waste.

For reference, a material flow sheet is shown in Figure 5.3.1.

5.4 Equipment Items Other Than Digester

A number of equipment items will be common to both the process for acid generation and to the process for generation of methane from municipal wastes, which has been discussed previously (Ref. 5.1-5.3). These include the receiving area, shredding, and other items such as pumps, piping, electrical and instrumentation. It is assumed that spent material may be returned to the algal growth system after the conversion process. Thus a vacuum filter will not be required.

5.5 Economic Evaluation of the Acid Generation Step

Since methods for recovering pure acids from dilute product streams are under development (discussed later) and costs are not readily available, the economic analysis will deal specifically with the cost of generating the acids in a dilute aqueous stream at a concentration of 0.15 to 0.25M.

The packed bed digester costs are a prime concern since this is the largest single item of capital equipment. Because this reactor may be of simple construction, that is, simple large tanks through which liquid circulates, or perhaps even lined, covered pits, the cost is estimated at 1.00/ft³ or \$4,550,000. Documented capital costs of other equipment items are taken from Refs. 5.1-5.3 and shown in Table 5.5.1. Total capital cost is estimated at \$11,400,000.

Figure 5.3.1

MATERIAL FLOWS IN PROCESS FOR ORGANIC ACID
PRODUCTION FROM MARINE ALGAE

Table 5.5.1

ESTIMATE OF CAPITAL REQUIREMENT FOR ALGAE TO
ORGANIC ACID FACILITY (ACID GENERATION ONLY: DOES NOT
INCLUDE RECOVERY OR FEEDSTOCK COSTS - SEE TEXT)

<u>Item</u>	<u>Estimated Cost</u>
Site Preparation	\$ 300,000
Receiving Area	111,500
Shredding	300,000
Building	300,000
Algae/Sludge Mixing	100,000
Packed Bed Digestion	4,550,000
Pumps and Piping	100,000
Instrumentation	100,000
Screw Conveyors	600,000
Bulk Solids Storage	<u>250,000</u>
	6,711,500
Constructor's Overhead, Profit (12%)	805,380
Engineering and Design (6%)	<u>402,690</u>
Subtotal Plant Investment	7,919,570
Project Contingency (15%)	1,180,935
Development Contingency (7)	<u>854,370</u>
Total Plant Investment	9,662,000
Interest During Construction (12%; 1.5 yr)	<u>1,739,160</u>
TOTAL CAPITAL REQUIREMENT	<u><u>\$11,401,160</u></u>

Operating costs are estimated to be similar to those for a solid waste to fuel gas plant, as described in References 2 and 3, or \$4,600,000/yr. It is to be noted that this cost estimate from References 2 and 3, applying to solid waste digestion, is inclusive, including labor, all utilities and taxes and insurance. In addition, it includes the cost of landfilling of inerts, as well as the major cost (over 40% of the total) of disposing of the solid undigested residue by incineration. The approximation is made with this assumed cost that labor, all utilities, taxes and insurance are identical for the two processes, and that the cost of disposing of solid waste in the digestion process equals the cost of returning the spent algal residue to the algal growth system. The operating cost does not include any credit for sludge disposal, and would be reduced in practice by any credit for this. It is also to be noted that this operating cost does not include provision for either feedstock or recovery. The effects of these are discussed later.

The cost of generating the acids in the form of a dilute stream is computed in Table 5.5.2 using the American Gas Association synthetic gas cost calculation method modified for the acid production process. The computation assumes a 75%/25% debt/equity ratio, 9% interest on debt, 15% return on equity, and 20 year straight-line amortization. Capital and operating costs are as estimated above. The cost of generating 263 MM lb of acids in dilute form yearly is computed to be 2.33¢/lb, to be compared with a market price of 18¢/lb for acetic acid. This extremely favorable cost of production relative to the current selling price of acetic acid simply reflects that organic acids are much higher value added products, per unit substrate feed, than are fuels such as methane. For example, if acetic acid were to be converted to methane, at \$0.0233/lb, the cost component due to acid feedstock alone would be over \$4.00/MCF produced. As noted, this favorable cost for production of dilute acids does not include cost for the feedstock. Separation and purification must also, of course, be economic in order to assure that acid production from marine algae is

feasible. However, separation costs in the range of those cited in the literature (Ref. 5.4) appear quite tolerable. Potential separation technologies are discussed in a later section.

5.6 Energy Balance of the Process

An important factor in any process to produce a fuel from biomass is the energy balance, that is, the ratio of energy produced/energy consumed by the process. This is also true of a petroleum feedstock sparing process to produce an organic chemical. In the case of acetic/organic acid production from marine algae, the energy balance may be expressed as the ratio of chemical feedstock energy spared to the energy required to run the process.

Estimated process energy requirements are shown in Table 5.6. Volumetric flows of material, both liquid and slurry, are considerable for the process, and the pumping and miscellaneous power requirement are estimated by assuming that the 46,000 Ton/day flow representing both input flow of algal slurry and liquid going to and from extraction undergoes a pressure drop of 50 psi. Although this is clearly an approximation requiring further refinement, pumping energy with this assumption is reasonable. With a 30% thermal-to-mechanical conversion efficiency to supply mechanical power requirements and an 85% heat transfer efficiency to satisfy heating requirements, the total energy requirement of the process is estimated to be 25.1×10^{10} BTU/year (90% plant service factor) with mesophilic operation. To manufacture 131,000 Tons/year acetic acid would require 87,500 Tons/year CO and 86,500 Tons/year CH_3OH , assuming respectively 70% and 90% process yields on those feedstocks from information in Reference 5.5. The gross or higher heating value for feedstock alone, not counting processing energy, will be 240×10^{10} BTU/year. This calculation shows the energy balance for the biological process over 9/1, that is, for each BTU of energy required to generate dilute acids with the process over 9 BTU of fossil feedstock

Table 5.5.2

COST OF PRODUCING DILUTE ACIDS

The cost for generating the dilute acid stream is computed using the American Gas Association Calculation Method for Synthetic Fuels as utilized in Ref. 5.3, adapted to the cost of producing organic acids.

$$\text{Average Production Cost} = \frac{N + 0.05 (C - W) + 0.005 \left[p + \frac{48}{52} (1 - d) r \right] (C + W)}{1}$$

where	N = Yearly operating cost; \$/yr	4,600,000
	C = Total capital requirement	11,400,000
	W = Working capital (1 mo. op. cost)	384,000
	P = Annual product, lb/yr	263,000,000
	p = Return on base rate, $d(i) + 1-d)r$, %/yr	10.5
	d = Fraction debt	0.75
	r = Return on equity, %/yr	15
	i = Interest on debt, %/yr	9

Average Production Cost = \$0.0233/lb acid (90% Plant Service Factor).

Does not include feedstock or recovery (see text).

The first term on the right-hand side represents the total net cost of operating the facility. The second term is the 5% per year straight-line depreciation on the total capital requirement excluding the working capital. The last expression includes terms for both the return on rate base and the federal income tax. The sum of all these terms is the total yearly revenue requirement, which, when divided by the annual production in pounds yields the average production cost in \$/lb.

energy are spared. Although the energy required for separation and purification will obviously increase the energy use, an energy requirement for separation and purification equal to that for production of the dilute acid stream would still leave an estimated favorable energy balance near 5:1.

5.7 The Acid Separation and Purification Step

The foregoing has dealt only with the engineering analysis and economics of the dilute acid generation step, technical feasibility of which is being established. The necessary separation and purification of acetic acid from this dilute product stream must rely on technologies for which up-to-date economics are not available. It is worthwhile, however, to mention briefly two recovery methods which might be applied.

Communications with Rohm and Haas Chemical Company, Philadelphia PA (Mr. Chester Fox) indicate that a modified version of their phenol recovery system has been laboratory tested for recovery of dilute low molecular weight organic acids (4000 PPM, principally butyric) in a process waste stream. The basis of this technology is acid absorption on a polymer column (breakthrough is less than 1 PPM) at a pH slightly below the pK_a of the acid stream or about 4.5. Following the absorption step, acid is eluted with methanol to give a stream containing 50% methanol, 25% acids and 25% water. Methanol is then washed off with water (99%⁺ total recovery) and methanol and acids are purified in separate distillation steps, the methanol for re-use in the process. Rohm and Haas has investigated the process on a laboratory scale; however, it is important to note that a similar process for recovering phenol (10,000 PPM) from a waste stream has been in commercial operation for over a year. Phenol recovery is reported profitable by this method.

Helsel, in a recent article in Chemical Engineering Progress (Ref. 5.4) presents an overview of another process for acetic acid recovery

Table 5.6

ENERGY REQUIREMENT OF ALGAE TO ACID FERMENTATION

A. Process Heat

Based on experience with solid waste fermentation to methane, the sole significant process heat requirement will be that to heat incoming material to the process temperature. The process heat required for acid generation is that needed to raise 6260 TPD input material ($C_p = 1$) from a baseline temperature of 55°F to 98°F (mesophilic operation) at 85% efficiency and is

$$6.26 \times 10^3 \text{ TPD} \times 2 \times 10^3 \text{ lb/ton} \times 43^\circ\text{F} \times 1 \text{ BTU/lb}^\circ\text{F} \times 330 \text{ days/year} \times 1/.85 \text{ efficiency} = 20.9 \times 10^{10} \text{ BTU/year.}$$

B. Heat Requirement to Produce Mechanical Power

Equipment items and estimated power requirements are as follows:

<u>Item</u>	<u>Time Average Power Requirement, hp</u>
Shredder	300
Mix Tank	100
Pumping and Miscellaneous (see text)	<u>225</u>
TOTAL	625

Heat requirement at 30% thermal conversion efficiency =

$$6.25 \times 10^3 \text{ hp} \times 2.545 \times 10^3 \text{ BTU/hp hr} \times 24 \text{ hr/day} \times 330 \text{ days/yr} \times 1/0.3 \text{ efficiency} = 4.20 \times 10^{10} \text{ BTU/yr.}$$

$$\text{Total Thermal Requirement} = 25.1 \times 10^{10} \text{ BTU/yr.}$$

using Trioctylphosphine oxide, or TOPO, as an extractant. Few processing details are given and the process is proprietary. However, for the specific instance in which 90% of the acetic acid in a 200 gal/min waste stream is removed, reducing acetic acid from an initial concentration of 2.0% to 0.2% to produce 15×10^6 lb/yr of acetic acid, the article claims a total manufacturing cost of 6.3¢/lb. (Extraction trials with TOPO are being carried out as a part of this experimental program.)

5.8 Influence of Feedstock Cost and Conversion Efficiency on Dilute Acid Cost

The cost increment imposed on acids (in dilute form) by the feedstock cost is simply C_F/Y , the feedstock cost divided by the yield of acid on feedstock. Assuming, for example, the constraint that the cost of feedstock should not represent more than one-third of the current market price of 18¢/lb, or 6¢/lb acid, then a Y of 0.35 (neglecting sludge) as in the preceding analysis would require a feedstock cost of not over \$42/ton. With this same constraint, a C_F of \$60/ton would require Y above 0.5, while a Y of 0.25 would require a C_F below \$30/ton. It would appear on the basis of this (quite elementary) analysis that a combination of feedstock cost and yield will be found such that the feedstock cost component is reasonable.

REFERENCES
(to Section 5)

- 5.1 Kispert, R.G., Anderson, L.C., Walker, D.H., Sadek, S.E., and Wise, D.L., "Fuel Gas Production From Solid Waste", Semi-Annual Progress Report on NSF Contract C-827, July 31, 1974.
- 5.2 Kispert, R.G., Sadek, S.E., and Wise, D.L., "An Economic Analysis of Fuel Gas Production from Solid Waste," Resource Recovery and Conservation, 1, 95 (1975).
- 5.3 Pfeffer, J.T. and Liebman, J., "Biological Conversion of Organic Refuse to Methane," Report on NSF Grant GI-39191, Department of Civil Engineering, University of Illinois at Urban-Champaign, September, 1975.
- 5.4 Helsel, R.W., "Removing Carboxylic Acids from Aqueous Wastes", Chemical Engineering Progress, May, 1977, p. 55.
- 5.5 Ellwood, P., Chemical Engineering, May 14, 1969, p. 148.

Section 6

PROGRAM FOR THE SECOND QUARTER

6.1 Determination of the Total Available Reducing Equivalents For Acid Production from *Chondrus Crispus* and Other Substrates.

This determination will be performed in the low solids unstirred fermenters currently in operation, or by total conversion experiments at higher solids levels once an acid removal system is developed, or by indirect methods.

6.2 Development of An Acid Removal System.

Work will continue on the development of a solvent extraction system to remove product acids, with a secondary effort on anion exchange. These experiments will be conducted in the four foot fixed packed bed fermenters currently in operation.

6.3 Additional Experiments in Unstirred Fermenters to Increase Initial Rates, Improve A/T Ratios, and Increase C_{∞} Values.

These experiments will be conducted using effluent from successful fermenters to inoculate new fermenters. Other marine algal substrates, e.g., *Gracillaria* and *Ulva lactuas* will be evaluated.

6.4 Construction of a Large Fixed Packed Bed Fermenter

A fixed packed bed fermenter approximately 1 foot in diameter and 15 feet in length will be constructed for use in scaleup experiments in the following quarter.